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Trace Elements Identification in KCl and NaCl using Laser-Induced Breakdown Spectroscopy

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Abstract *Infrared laser-induced breakdown spectroscopy (IR-LIBS) was used for trace element identification of potassium (K) and sodium (Na) in samples of potassium chloride (KCl) and sodium chloride (NaCl) respectively. IR LIBS spectra of KCl and NaCl exhibited atomic transitions within the mid-wavelength (2–5 μm) IR region consistent with atomic transitions obtained from the National Institute of Standards and Technology (NIST) atomic spectra database. Observed transitions for potassium were 2.71, 3.14, 3.16, 3.18, 3.73, 3.75, and 4.02 μm while those for sodium were 2.30, 2.34, 3.42, 4.05, and 4.38 μm. However, from the observed transitions profile, those at 2.71 μm (for potassium) and 2.20 μm (for sodium transitions) exhibited strong intensity and provided a reference for-establishing IR-LIBS as a viable spectroscopic technique for trace elements identification in hybrid substances.*

Keywords: *IR-LIBS, trace elements, breakdown spectroscopy, atomic spectra, atomic transitions*

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1.0 Introduction

Spectroscopy is the study of interaction of radiation with matter. Although there are several types of spectroscopy available for analytical purposes, little attention is paid to breakdown spectroscopy. Breakdown spectroscopy is an analytical technique in which the emission of electromagnetic radiation is produced by excited atoms, ions or molecules contained in a substance (Gonzaga & Pasquini, 2008). The technique ~~usually~~ involves the breaking down of the sample or analyte into its constituent atoms, ions or molecules by the application of an excitation energy source such as a laser source, which promotes these particles into their excited states, from where they decay and emit radiation characteristic of each particle (Pasquini *et al.*, 2007), hence the name Laser-Induced Breakdown Spectroscopy (LIBS). LIBS is an atomic emission spectroscopy technique that uses a highly energetic laser as the source of excitation. Potassium and sodium belong to group one in the periodic table indicating that their ionization energies are low. Sodium, for example has a 1st ionization energy of 496 kJ/mol while potassium has a 1st ionization energy of 425 kJ/mol. Spectroscopic methods normally used for their analysis is flame ionization spectrophotometry. This method often requires sample preparation and may be characterized by several interferences; hence the results may not be too precise. However, LIBS do not require sample preparation and is sensitive to trace concentration analysis. LIBS has emerged as a viable technique for investigating trace elements in materials, making its debut appearance in the visible and near infrared

emission bands. (Radziemski *et al*., 2007), with research focusing mainly on atomic and molecular measurements in the UV-NIR (200-980 nm) region. LIBS instrumentation involves not only the excitation of the constituents of the target substance but also the collection and analysis of the resulting emission. From start to finish, a LIBS event consists of the excitation of the target substance by a highly focused intense laser beam to produce a hot, short-lived plasma, which on cooling produces emission at different wavelengths that identify the constituent atoms or ions (Cremers & Radziemski, 2013). The development of the LIBS technique has improved over the years with advancements in laser technology as well as fluorescence detection techniques. Time resolved LIBS using charge-coupled device (CCD) detector has been reported by Vadillo *et al.* (1996) while Davis *et al.* (1993) reported the result of using 60 ps Nd:YAG 532 nm pulses for the LIBS event. Within the UV-NIR wavelength region, LIBS spectroscopy has been used for geochemical and environmental analysis. For example, Harmon *et al*., (2005) observed NIR LIBS spectrum of 725-975 nm for air, as well as a broadband LIBS spectrum between 200 and 1000 nm for quartz in air, with various peaks of silicon, oxygen, and nitrogen identified. The LIBS technique has been employed in the UV region for the determination of manganese content in steel (Gonzaga & Pasquini, 2008) and for quality assurance in the industrial production of steel (Noll *et al*., 2001). Detection limit studies have been carried out as well in the UV-VIS-NIR spectral region. Mohamed, (2008) observed the LIBS emissions wavelength of of aluminum in aluminum alloy between–200-1000 nm spectral range and found that the technique accurately gave the concertation of aluminum in the alloy.

Based on the well-known fact that molecules exhibit spectroscopic signatures in the mid-IR region due to molecular vibrational and rotational transitions, Yang *et al.* (2007), undertook the first mid-IR LIBS on solid state organic and inorganic materials. They observed for the first time, mid-IR molecular emissions of the laser-induced breakdown products of some solid organic substrate (i.e, CO and CO_2 molecules) . They also observed LIBS mid-IR atomic line emissions from alkali metal halides solid tablets between 2 and 5.6 μm (Yang et al., 2008).

Following the pioneering work by Yang *et al.* (2007), further spectroscopic studies were conducted on potassium chloride (KCl) and sodium chloride (NaCl) pellets for both mid-IR (2-5 μm) and long wavelength-IR (5-10 μm) spectral regions. In this work, we present the LIBS spectra of KCl and NaCl in the mid-IR (2-5 μm) spectral region. The LIBS spectra in the long wavelength-IR (5-10 μm) spectral region has been reported elsewhere (Oyebola *et al*., 2017). In the current study, our focus is in the mid-IR region which can complement the well-established UV-VIS LIBS technique in trace element identification. Some studies have been reported on the use of LIBS technique to analyze trace elements in food, geological and other samples. Kim *et al.* (2019) used LIBS to detect trace concentrations of magnesium and calcium ions in edible salts, which were below the detection limit for other spectroscopy methods. Yonghoon, L. and Han (2017) also reported similar findings for the analysis of magnesium, calcium and potassium in samples of some edible salts. They concluded that the LIBS is a feasible method than any, in analyzing magnesium and calcium in edible salt. Qu *et al.* (2016) however used tunable diode Laser atomic absorption spectroscopy for detection of potassium under optically thick conditions. Ng & Cheung (2000) found that Laser ablative sampling was a feasible method for detecting sodium and potassium ion in single human red blood cells, Singh *et al*. (2009) used obtained LIBS spectra of different salt samples (including potassium, sodium, calcium, etc) in the spectral region 200–500 nm with spectral resolution 0.1 nm and in the spectral region 200–900 nm with spectral resolution 0.75 nm. Lee *et al.* (2016) used Laser-induced breakdown spectroscopy and laser ablation inductively coupled plasma mass spectrometry analysis to analyze trace metals in edible salts (including sodium, potassium, calcium, magnesium, etc). In continuation of researches in the feasibility of LIBS for trace metal analysis, the present study is aimed at the mid-IR (2-5 μm) spectral region. To the best of our knowledge, spectroscopic study KCL and NaCl in the mid-IR has not received sufficient scientific attention in the literature.

2.0 Materials and Method

The schematic diagram of the IR-LIBS experimental setup has been reported elsewhere (Oyebola et al.,

2011). The target samples of KCl and NaCl were excited with a Q-switched Nd:YAG pulse laser with 5 ns pulse width, 10 Hz repetition rate and 1064 nm output. The laser pulse energy in the range 30 to 40 mJ was used. It was necessary to use solid samples with flat surfaces for the initial IR-LIBS experiments. Powder samples were pressed into pellets of fairly equal sizes using a standard bench top pellet press (hydraulic press). The sample was mounted on a linear translating stage attached to a stepper motor operated by a controller, which allowed the sample to be translated at a speed of about 1.5 mm/min (Yang *et al*., 2007). This ensured that the laser pulse hit a fresh spot on the sample during each emission scan. The specified speed was chosen to limit the spectral scan to the size of the sample pellet. Several scans were made at 100 nm/min, in segments of 1200 nm within the spectral range under investigation.

The resulting IR emission was collimated into a 0.15 m grating spectrometer through a long pass filter suitable for the spectral range under investigation. The signal was detected with an indium antimonide (InSb) detector for the mid-IR spectral range (2-5 µm) and a mercury cadmium tellurium (MCT) detector for the far-IR spectral range (5-10 µm). The two detectors were liquid nitrogen cooled. The spectrometer grating was set at 4 µm, 150 grooves/mm, for the mid-IR, and 8 µm, 75 grooves/mm, for the long-IR wavelength ranges. The entrance and exit slits of the spectrometer were kept at a width of 0.25 mm with a spectral resolution of 3.128 nm, except during the detection limit experiments when they were opened up to 1.0 mm. The detected signal was analyzed on a computer through an integrated boxcar averager set at 10 µs gate delay and 16 µs gate width.

Under the described experimental conditions, KCl and NaCl pellets were scanned separately between 2 and 5 µm and atomic emission lines corresponding to potassium in KCl and sodium in NaCl were observed using the liquid nitrogen cooled InSb detector. In order to use appropriate filters, it was necessary to split the 2-5 µm range into two scan ranges. The first scan was from 2 to 3.2 µm at 100 nm/min, using the LP2000 filter and the second was from 3.2 to 4.4µm at 100nm/min, using the LP3000 filter.

3.0 Results and Discussion

The LIBS spectra for KCl and NaCl are shown in Fig. 1 while the transition assignments for the dominant potassium and sodium emissions (obtained from the NIST Atomic Spectral Database) are shown in Table 1 (Kramida et al., 2019). Similar transition assignments for KCl and NaCl were reported by Yang *et al*. (2007) as shown in Table 1. Emission from chlorine atom was neither observed in this work nor reported elsewhere, including the NIST Atomic Spectral database (Kramida *et al*., 2019). The observed emission peaks are consistent with the literature values as given in the NIST database as well as those published by Yang *et al.* (2007).

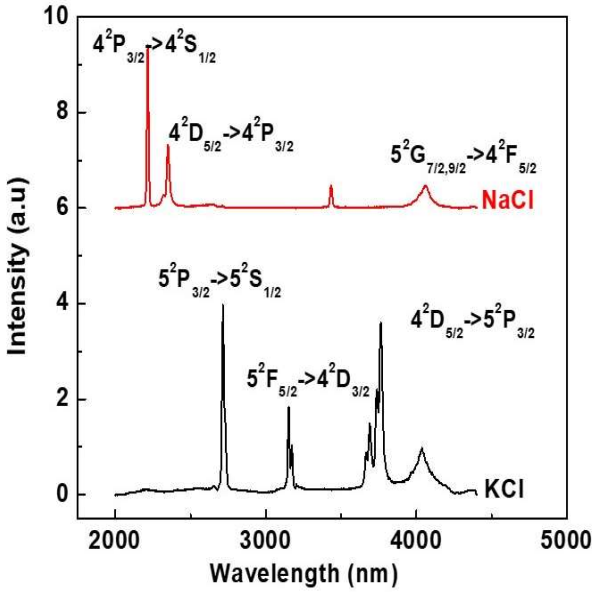

Fig. 1: Overview IR-LIBS spectra for KCl and NaCl in the 2-5 µm region.

The emission lines listed by NIST correspond to lines that appear in the spectrum of neutral and ionized potassium and sodium excited in an electrical discharge. Their assignments are determined based on their calculated transition probabilities, a quantum mechanical process (Hu *et al.*, 2015). There are several potassium and sodium lines within the scanned mid-IR range but the assigned transitions were based on the transitions with the highest transition probabilities for neutral potassium and sodium. The potassium and sodium

emissions at 2.72 and 2.21μm, respectively, are particularly strong, which considerably reduced the effect of any possible water or carbon dioxide absorption within that spectral region.

Table 1. Transition assignments of K and Na atomic transitions in the 2-5μm range.

	λ, μm (Observed)	λ, μm (Literature) [NIST]	λ, μm (Yang *et al*]	Transition Probability (s^{-1})	Assigned Transition	E_i (cm^{-1})	E_j (cm^{-1})
K	2.71	2.70	2.71	4.6×10^6	$5^2P_{3/2} - 5^2S_{1/2}$	21026	24720
	3.14	3.11	3.15	1.9×10^6	$5^2F_{5/2} - 4^2D_{3/2}$	27398	30606
	3.16	3.16	3.18	1.5×10^6	$5^2P_{1/2} - 3^2D_{3/2}$	21536	24701
	3.66	3.63	3.65	1.6×10^6	$6^2S_{1/2} - 5^2P_{1/2}$	24701	27450
	3.68	3.66	3.68	3.2×10^6	$6^2S_{1/2} - 5^2P_{3/2}$	24720	27450
	3.73	3.70	3.73	2.9×10^6	$4^2D_{3/2} - 5^2P_{1/2}$	24701	27398
	3.75	3.74	3.76	3.4×10^6	$4^2D_{5/2} - 5^2P_{3/2}$	24720	27397
	4.02	4.02	4.03	No Data	$5^2G_{7/2,9/2} - 4^2F_{5/2}$	28127	30617
Na	2.20	2.21	2.21	6.64×10^6	$4^2P_{3/2} - 4^2S_{1/2}$	25739	30272
	2.34	2.34	2.34	7.01×10^6	$4^2D_{5/2} - 4^2P_{3/2}$	30272	34548
	3.42	3.41	3.42	3.6×10^6	$5^2S_{1/2} - 4^2P_{3/2}$	30272	33200
	4.05	4.04	4.05	No Data	$5^2G_{7/2,9/2} - 4^2F_{5/2}$	34586	37059

Transition probabilities are a measure of the emission intensities. In the KCl sample, the transitions centered at 2.71, 3.68 and 3.75 μm are the dominant transitions for potassium as indicated in Fig. 1 and corroborated by their high transition probabilities. For NaCl, the dominant transitions for sodium are centered at 2.2 and 2.34 μm. The transition probability of the emission centered at 4.04 μm was not shown as its intensity is shared by several lines (Kramida *et al.*, 2019). These transitions are the signatures to look for in tracing sodium or potassium in hybrid materials.

The wavelength calibration of the 2-5 μm region was done by monitoring the well-known CO_2 absorption that falls within this range. This was done by taking the spectrum of a standard MIR Lamp (15A Orion OL550 lamp) under the same IR LIBS setup conditions. The wavelength of CO_2 absorption was measured and compared to its standard data. The measured absorption wavelength was 4270 nm as shown in figure 2, while the standard wavelength of CO_2 absorption is known to be 4255 nm (Primrose, 1946). Hence a factor of 15 nm was subtracted from the measured IR-LIBS emission wavelengths in this spectral range. It must be noted, however, that the wavelength correction might not necessarily be uniform throughout the covered spectral range. A more accurate calibration would require the measurement of several wavelengths within the spectral range where standard data are available, so that a calibration function can be generated and applied across the spectral range. The current calibration based on the CO_2 absorption has, however, produced IR-LIBS data for potassium (K) and sodium (Na) that are very close to the NIST data as shown in Table 1.

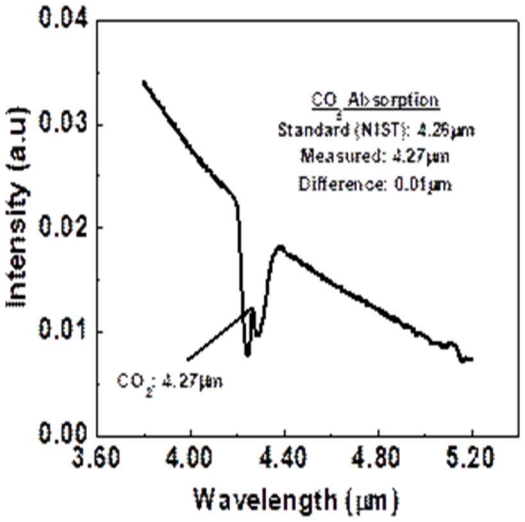

Fig. 2: Spectrum of MIR lamp showing the CO_2 absorption band.

4.0 Conclusion

Mid-IR LIBS spectra of potassium chloride (KCl) and sodium chloride (NaCl) were observed showing distinct K and Na atomic transitions within the 2–5 μm wavelength range. The observed emissions and their assigned transitions are consistent with the NIST data of atomic transitions. The 2.71 μm potassium and 2.20 μm sodium transitions are particularly strong and can be explored for trace elements identification in hybrid substances where they appear. The Mid IR-LIBS technique has proven to be a worthwhile compliment to the well-established UV-VIS LIBS technique in trace element identification. Further improvements in LIBS instrumentation and experimental conditions are expected to yield higher sensitivity and sharper spectral resolutions. For example, an improvement of the sample mount translation technique could result in IR LIBS spectra that exhibit an increased reproducibility.

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